

AGROCHEMICAL COMPOSITION CONTAINING
PHOSPHITE AND PROCESS FOR THE PREPARATION
THEREOF

EPO - DG 1

08.09.2004

5 **Field of the Invention**

(96)

This invention relates to a solid, granular and uniform in the particle size, free flowing, water-soluble, agrochemical composition, containing phosphite and being homogeneous in the chemical composition, that contains at least one other NPK nutrient, and comprises metal
10 microelements.

Background of the Invention

An ideal agrochemical composition would provide all elements necessary for the plant growth, it would provide some protection against pests, and it
15 would not leave harmful or useless deposits in the soil. Such composition should be further easy for storage, manipulation, usage, and marketing. From the aforesaid results that an ideal composition should be solid, particulate but not dusty, and water-soluble.

20 Phosphites are used in agrochemical compositions as a phosphorus source and for their pesticidal potential. Publication WO 00/76941 claims potassium phosphites as a fertilizer for trees, vines and crops. U.S. Patent No. 5,514,200 teaches that phosphite fertilizers inhibit the beneficial symbiosis between plant roots and mycorrhizal fungi, and further promote

BEST AVAILABLE COPY

AMENDED SHEET

bacterial and fungicidal growth. The U.S. patent No. 5,830,255 discloses a concentrated buffered phosphorus fertilizer comprising a phosphorous salt or acid, and possibly other nutrients. Fertilizer compositions for plants containing phosphite (PO_3^{3-}) and phosphate (PO_4^{3-}) salts are disclosed in 5 U.S. Patent No. 5,800,837, and antifungal compositions containing phosphite and phosphate salts are disclosed in WO 01/28334. U.S. Patent No. 5,736,164 relates to a composition which contains phosphite and phosphate salts and derivatives thereof for controlling parasitic fungi, and U.S. Patent No. 4,119,724 discloses fungicidal compositions containing 10 phosphorous acid and inorganic and organic salts, as well as a method for their application to plants for controlling fungus disease.

It is desirable to provide a phosphite containing agrochemical composition that would also possess the above mentioned advantageous physical 15 properties. It is therefore an object of this invention to provide an agrochemical composition that is solid, granular and uniform in the particle size, and water-soluble, contains phosphite and is homogeneous in the chemical composition, which composition contains at least one other NPK nutrient (nitrogen and/or phosphorus and/or potassium containing 20 nutrient), and comprises metal microelements.

It is a further object of this invention to provide a process for manufacturing said agrochemical composition.

-3-

Other objects and advantages of present invention will appear as description proceeds.

5

Summary of the Invention

This invention provides an agrochemical composition that is solid, granular and uniform in particle size, free flowing, and water-soluble, and contains phosphite and is homogeneous in the chemical composition, 10 which composition contains at least one other NPK nutrient, and comprises metal microelements. The invention provides a process for manufacturing said agrochemical composition, which process is characterized in that it comprises i) blending and heating at a temperature from 60°C to 130°C a mixture containing phosphorous acid, 15 at least one other NPK nutrient, metal microelements and other additives enhancing its fertilizing and pesticidal properties or modifying functional or aesthetic properties of the particles; ii) introducing a base into the mixture, thus at least partially neutralizing phosphorous acid, wherein the amount of the base is sufficient to provide that the pH of a 1% 20 water solution of the final composition will be between 3.4 and 7.0; iii) homogenizing the mixture, while optionally lowering the pressure above the mixture; iv) and cooling the mixture, while obtaining a homogeneous, granular, free flowing and not caking material, with low hygroscopicity, containing from 0% to 1% water.

Detailed Description of the Invention

It has now been found that phosphite salts, NPK nutrients, and metal microelements can be combined in a homogeneous agrochemical composition that has a consistency of solid, granular and particle-size uniform, and water-soluble material. The present invention provides a process for obtaining such composition comprising i) blending and heating a mixture containing phosphorous acid, at least one NPK nutrient, and metal microelements and other additives; ii) introducing a base into the mixture, thus partially neutralizing phosphorous acid, wherein the amount of the base is sufficient to provide that the pH of a 1% water solution of the final composition will be between 3.4 and 7.0; iii) homogenizing the mixture, and optionally lowering the pressure above the mixture; iv) and cooling the mixture, breaking it up, and obtaining a dry, granular, homogeneous material.

15

The components may be added to the mixture, or may be preheated, in any order. However, the complete mixture must be heated at a temperature between 60°C and 130°C, becoming molten and enabling good homogenization. In one embodiment, all the components are blended and preheated in a reactor to 100°C, followed by adding solid phosphorous acid into the mixture, incubating the mixture until a paste is obtained, and homogenizing the mixture when the viscosity decreases. In another

20

embodiment, phosphorous acid is first heated at a temperature higher than 60°C, and all other ingredients are then added to the molten acid.

The NPK nutrient is preferably chosen from the group consisting of
5 monoammonium phosphate, monopotassium phosphate, dipotassium phosphate, sodium nitrate, potassium chloride, ammonium chloride, potassium sulfate, ammonium sulfate, and urea. The metal microelements are preferably chosen from the group consisting of zinc, copper, iron, manganese, molybdenum, and boron, and can be added as a compound
10 contained in any commercially available material. Metals can be present as cations in salts such as chloride, nitrate, sulfate; as anions such as molybdate; as chelates such as ethylenediamine tetraacetate, or other, such as boric acid.

15 The ratios between phosphorous, other NPK nutrients, and the micronutrients, are determined according to their required relative content in the final product.

The amount of phosphorous acid in the mixture according to this invention
20 is from 10 to 95 wt%, the amount of other NPK nutrients is between 5 to 90 wt%, and the amount of microelements is from 0.005 wt% to 2 wt%. In a preferred embodiment of this invention, monoammonium phosphate (MAP) and monopotassium phosphate (MKP) are used as other NPK

nutrients. In one embodiment MAP, MKP and phosphorous acid are used in ratios 1:2:1. In another embodiment only MKP as another NPK nutrient beside phosphorous acid is used, wherein the ratio MKP to phosphorous is 3:1.

5

The molten mixture is at least partially neutralized by a base, wherein the amount of the base is chosen as to ensure a pH from 3.4 to 7.0 for the final product in 1% water solution. This pH is optimal from viewpoint of i) the hygroscopicity of the final composition, ii) the solubility of the composition,
10 and iii) the fertilizing and pesticidal effect of the composition during its use. Said pH confers the composition according to this invention a relatively low hygroscopicity, as expressed by the critical relative humidity, which is typically from 50% to 65%, and more typically from 55% to 60%.

15

In a preferred embodiment of this invention, a base MR is chosen from carbonates and hydroxides, wherein M is selected from K^+ , NH_4^+ and R is selected from CO_3^{2-} and OH^- . In a still more preferred embodiment, the base comprises potassium carbonate or potassium hydroxide. In some
20 embodiments of this invention, the neutralization reaction can be summarized as:



During the neutralization, the temperature can increase due to the release of the neutralization heat, aiding the homogenization process. The homogenization of the molten mixture is eventually accompanied by formation of water and/or carbon dioxide inside the viscose material, and
5 by their escape to the gas phase. In a preferred arrangements of the process according to this invention, the pressure above the molten mixture is lowered, which accelerates removal of water from the mixture.

In a preferred embodiment of this invention, the molten mixture before
10 the neutralization is heated at a temperature 61°C to 100°C. In another embodiment according to this invention, the pressure above the molten mixture is lowered below 70 mm Hg, and preferably below 40 mm Hg.

The homogeneous molten mixture is finally cooled, and broken up. The
15 consistency of the cooled material enables to obtain a granular, free flowing, material with uniform grain-size by using methods known in the art. The particles contain typically less than 1 wt% water, and more typically from 0.1 to 0.4 wt% water.

20 An agrochemical composition according to this invention is completely dissolved when mixing 10 parts of the composition with 90 parts of water at an ambient temperature. Said composition provides pH from 3.4 to 7.0, and more typically pH from 3.8 to 5.3, when dissolved 1 part in 100 parts

of water. A typical composition of this invention dissolves completely even in the ratio of 20 parts per 80 parts of water, when mixed at ambient temperatures.

- 5 An agrochemical composition according to this invention may additionally contain additives that further enhance its fertilizing and pesticidal properties, such as humic acid, or that modify functional or aesthetic properties of the particles finally obtained, such as surfactants or dyes.
- 10 The invention will be further described and illustrated in the following examples.

Examples

Materials

- 15 Monopotassium phosphate and monoammonium phosphate, used here, are products of Rotem Amfert Negev Ltd., Israel.

General procedures

- The samples of granular compositions were prepared in either of two stirred reactors, equipped with heating and cooling mantle, having
20 volumes 1 and 5 liters, respectively. The smaller one was a glass reactor, and the bigger one a steel reactor equipped with a condenser, and connected to a vacuum pump. The solubility of the samples was

characterized by mixing 10 gram in 90 ml distilled water at room temperature for 1 hour. A 1% solution was used for pH measurements. The water content of compositions was determined using Mettler balance adopted for humidity measurements. The hygroscopicity was characterized as the critical relative humidity, as per T.V.A. standard. Shortly, this method determines a relative humidity of an environment in which water absorption by the sample causes a mass increase higher than 3%. The size distribution was characterized by measuring mass fraction of the particles having size less than 0.25 mm, between 0.25 and 1.4 mm, and more than 1.4 mm.

Example 1

A molten mixture was prepared in the glass reactor by mixing 80 g monopotassium phosphate (MKP) and 20 g phosphorous acid (PA). The mixture was heated, and the melting started at temperature 62°C. The molten mixture was neutralized by 20.8 g potassium carbonate, and the temperature reached 106°C. The molten mixture was cooled by feeding it to a cool medium, and crushed. A granular product was obtained, characterized by pH 3.8 in the 1% solution, and hygroscopicity expressed by the the critical relative humidity of 60-65%.

20

Example 2

A molten mixture was prepared as in example 1 by mixing 80 g MKP and 20 g PA. The mixture was heated, and the melting started at temperature

62°C. The molten mixture was neutralized by 21.2 g potassium carbonate, and the temperature reached 120°C. The molten mixture was cooled by feeding it to a cool medium, and crushed. A granular product was obtained, characterized by the pH 4.4 in 1% solution, and the
5 hygroscopicity expressed by the critical relative humidity of 55-60%.

Example 3

A molten mixture was prepared as in example 1 by mixing 80 g MKP and 20 g PA. The mixture was heated, and the melting started at temperature
10 62°C. The molten mixture was neutralized by 22.8 g potassium carbonate, and the temperature reached 106°C. The molten mixture was cooled by feeding it to a cool medium, and crushed. A granular product was obtained, characterized by pH 5.0 in 1% solution, and hygroscopicity expressed by the critical relative humidity of 50-55%.

15

Example 4

A mixture containing 66 g MKP, 21.5 g PA, and micronutrients comprising 2.0 g Mg EDTA and 0.5 g Mn EDTA, was heated in a glass reactor, and the melting started at temperature 62°C. The molten mixture
20 was neutralized by 18.7 g potassium carbonate, and the temperature reached 140°C. The molten mixture was cooled by feeding it to a cool medium, and crushed. A granular product was obtained, characterized by

pH 4.2 in 1% solution, and hygroscopicity expressed by the critical relative humidity of 55-60%.

Example 5

A mixture containing 66 g MKP, 21.5 g PA, and micronutrients
5 comprising 2.0 g Mg EDTA and 0.5 g Mn EDTA, was heated in a glass
reactor, and the melting started at temperature 62°C. The molten mixture
was neutralized by 13.1 g potassium carbonate, and the temperature
reached 130°C. The molten mixture was cooled by feeding it to a cool
medium, and crushed. A granular product was obtained, characterized by
10 pH 3.4 in 1% solution, and hygroscopicity expressed by the critical relative
humidity of 55-60%.

Example 6

A homogeneous blend of 252.9 g monoammonium phosphate (MAP), 497.5 g
monopotassium phosphate (MKP), 3.98 g Zn EDTA, and 2.03 g Cu EDTA
15 was placed in the steel reactor, heated to 100°C, and stirred for 10
minutes, followed by adding 205.4 g of solid phosphorous acid (PA). The
mixture acquired a consistency of paste, the viscosity of which decreased
with time. After 10 minutes 278.8 g of potassium carbonate was added to
the reactor, followed by release of heat, water and carbon dioxide, and
20 decrease of the viscosity. Stirring continued for 5 minutes. The mixture
was perfectly homogeneous. In order to increase the intensity of drying
after the sufficient homogenization, the vacuum pump was activated for
15 minutes, lowering the pressure to about 30 mm Hg. The crushed

material was then cooled. About 883 g of a granular, free flowing composition was obtained, having 72.8 % mass in the preferred size range of 0.25-1.4 mm, with 6.5% being smaller and 20.7% bigger. The water content of the composition was 0.44%, the pH of its 1% solution was 5.3, and its hygroscopicity as expressed by the critical relative humidity was 55-60%. No caking was observed.

Example 7

A homogeneous blend of 168.6 g MAP, 331.7 g MKP, 2.65 g Zn EDTA, and 1.35 g Cu EDTA was placed in the steel reactor, heated to 100°C, and stirred for 10 minutes, followed by the addition of 137 g of solid PA. The mixture acquired a consistency of paste, the viscosity of which decreased with time. After 10 minutes 172.5 g of potassium carbonate was added to the reactor, followed by release of heat, water and carbon dioxide, and decrease of the viscosity. Stirring continued for 5 minutes. The mixture was perfectly homogeneous. The vacuum pump was activated for 30 minutes, lowering the pressure to about 30 mm Hg. The material was then cooled, and crushed. About 631 g of a granular, free flowing, composition was obtained, having 74.8 % mass in the preferred size range of 0.25-1.4 mm, with 1.4% being smaller and 23.8% bigger. The water content of the composition was 0.17%, the pH of its 1% solution was 5.1, and its hygroscopicity, as expressed by the critical relative humidity, was 55%. No caking was observed.

Example 8

A homogeneous blend of 168.6 g MAP, 331.7 g MKP, 2.65 g Zn EDTA ,
1.35 g Cu EDTA, and 7.9 g humic acid was placed in the steel reactor,
heated to 100°C, and stirred for 10 minutes, followed by the addition of
5 137 g of solid PA. The mixture acquired a consistency of paste, the
viscosity of which decreased with time. After 10 minutes 172.5 g of
potassium carbonate was added to the reactor, followed by release of heat,
water and carbon dioxide, and decrease of the viscosity. Stirring continued
for 5 minutes. The mixture was perfectly homogeneous. The vacuum pump
10 was activated for 14 minutes, lowering the pressure to about 30 mm Hg.
The material was then cooled and crushed. About 630 g of a granular, free
flowing, composition was obtained, having 62.6 % mass in the preferred
size range of 0.25-1.4 mm, with 11.2% being smaller and 26.2% bigger.
The water content of the composition was 0.23%, the pH of its 1% solution
15 was 5.0, and its hygroscopicity, as expressed by the critical relative
humidity, was 55%. No caking was observed.

Example 9

A homogeneous blend of 168.6 g MAP, 331.7 g MKP, 2.65 g Zn EDTA ,
20 1.35 g Cu EDTA, and 20 g of stimulator Fertivant was placed in the steel
reactor, heated to 100°C, and stirred for 10 minutes, followed by the
addition of 137 g of solid PA. The mixture acquired a consistency of paste,
the viscosity of which decreased with time. After 10 minutes 172.5 g of

potassium carbonate was added to the reactor, followed by release of heat, water and carbon dioxide, and decrease of the viscosity. Stirring continued for 5 minutes. The mixture was perfectly homogeneous. The vacuum pump was activated for 23 minutes, lowering the pressure to about 30 mm Hg.

5 The material was then cooled and crushed. About 620 g of a granular, free flowing, composition was obtained, having 81.0 % mass in the preferred size range of 0.25-1.4 mm, with 2.5% being smaller and 16.5% bigger. The water content of the composition was 0.31%, the pH of its 1% solution was 4.8, and its hygroscopicity, as expressed by the critical relative humidity

10 was 55%. No caking was observed.

Example 10

A homogeneous blend of 168.6 g MAP, 331.7 g MKP, 2.65 g Zn EDTA , AND 1.35 g Cu EDTA, was placed in the steel reactor, heated to 100°C,

15 and stirred for 10 minutes, followed by the addition of 137 g of solid PA. The mixture acquired a consistency of paste, the viscosity of which decreased with time. After 10 minutes 292.2 g of 48% potassium hydroxide was added to the reactor. Stirring continued for 5 minutes. The mixture was perfectly homogeneous. The vacuum pump was activated for 45

20 minutes, lowering the pressure gradually to about 30 mm Hg. The mixture was then cooled and crushed. About 600 g of a granular, free flowing, composition was obtained, having 90.7 % mass in the preferred size range of 0.25-1.4 mm, with 0.6% being smaller and 8.7% bigger. The water

content of the composition was 0.36%, the pH of its 1% solution was 5.0, and its hygroscopicity as expressed by the critical relative humidity was 55%. No caking was observed.

Example 11

5 A homogeneous blend of 168.6 g MAP, 331.7 g MKP, 2.65 g Zn EDTA , 1.35 g Cu EDTA, and 100 mg of the violet dye Rhodamine was placed in the steel reactor, heated to 100°C, and stirred for 10 minutes, followed by the addition of 137 g of solid PA. The mixture acquired a consistency of paste, the viscosity of which decreased with time. After 10 minutes 172.5 g
10 of potassium carbonate was added to the reactor, followed by release of heat, water and carbon dioxide, and decrease of the viscosity. Stirring continued for 5 minutes. The mixture was perfectly homogeneous. The vacuum pump was activated for 22 minutes, lowering the pressure to about 30 mm Hg. The homogeneously violet material was then cooled and
15 crushed. A granular, free flowing, composition was obtained, having the water content 0.47%, pH 4.4 in 1% solution, and hygroscopicity 55%, as expressed by the critical relative humidity.

All the above has been provided for the purpose of illustration and is not
20 intended to limit the invention in any way, except as defined in the claims to follow. Many modifications can be effected in the materials and methods described above, without exceeding the scope of the invention.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.